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13. ABSTRACT (Maximum 200 Words) The key objectives of this research project were (i) to synthesize <i>fibers</i> from polymer derived silicon carbonitride, (ii) to measure and understand the chemical and structural stability at ultrahigh temperatures, and (iii) to measure the mechanical properties of the fibers. All have been realized. The synthesis of the fibers required innovative modification of a commercial precursor; a U.S. patent for this novel process has been filed. The fibers are shown to have excellent mechanical properties and to be stable up to 1350°C without a measurable change in their nanostructure (which is essentially amorphous). They are thermally stable (against decomposition) up to 1400°C. Interestingly the fibers are a composite of an oxide phase (zirconia) dispersed in the form of nanoscale particles in the polymer derived silicon carbonitride matrix. This novel discovery of oxide/non-oxide polymer-derived-ceramics (PDCs) is leading to new insights into the nanostructure and properties of these scientifically exciting materials. The PDCs are envisioned to emerge as technological important ultrahigh temperature materials for air and space applications.					
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FINAL PERFORMANCE REPORT

ULTRAHIGH TEMPERATURE SILICON CARBONITRIDE FIBER SCIENCE

F49620-00-1-0109

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Executive Summary

This final performance report contains a summary of the results obtained over a period of three years under an AFOSR Grant entitled, "Ultrahigh Temperature Silicon Carbonitride Fiber Science". The stated objectives in this project were ambitious. To put a perspective around the gains and achievements in this project, consider the status of this field, four years or so ago, then known as precursor ceramics. At that time the reports in the published literature were brief, describing mere observations suggesting that materials with apparently unusual high temperature properties could be fabricated from the pyrolysis of a certain class of organic precursors (silazanes). The materials so obtained contained silicon, carbon and nitrogen and were remarkably stable, showing resistance to crystallization and thermal degradation at ultrahigh temperatures. There were anecdotal, but unsubstantiated reports of the fabrication of fibers and outstanding resistance to oxidation. However, even elementary properties, for example the Young's modulus had not been measured, mainly because dense samples had yet to be synthesized. Today, and in a large measure as a result of the work carried out under this AFOSR Grant at the University of Colorado, the field of *polymer-derived-ceramics* or PDCs is starting to achieve credibility and scientific acceptance. The key achievements of the work carried out under this grant, which have contributed to the emergence of this new field, are as follows:

A. The development of a pressure casting process which enables the fabrication of dense, pore free samples of SiCN (silicon carbonitride), and the measurement of the Young's modulus and the fracture strength of this material. These dense samples have also led to the fundamental measurement of the oxidation behavior of PDCs.

B. A key paper on "nanoscale densification creep" of SiCN which reported experiments that measured the shear and densification creep simultaneously, and then showed that the shear component was nearly zero. A model for densification creep was put forward which showed excellent agreement with experiment. This model suggested that diffusion in these materials was very slow because the size of the diffusing unit was very large (1.2 nm).

C. The development of a fiber drawing process based upon modification of the SiCN precursor (a polysilazane) with oxide precursor (zirconium isopropoxide) in order to create a fiber-friendly rheology in the polymer mixture. The thermal and nanostructural stability of this oxide-nonoxide PDC was measured. The mechanical properties of the fiber have been characterized. The implications of this work are now reaching beyond "fiber science" because the nature of these oxide-nonoxide nanocomposites is beginning to provide new insights into the fundamental structure of the PDCs.

The work supported by this grant has led to *three* publications in 2001, *three* in 2002 and *four* more publications in 2003, all except one being published in the Journal of the American Ceramic Society. The exception was published in Acta Materialia. The work on fibers has been filed as a U.S. Patent. The work was presented at the Gordon Conference on Ceramic Science in summer 2002, both as invited presentation and as a poster. The poster, which focussed on the

PDC fiber won wide acclaim (it was initially selected as the best poster but then put aside since the primary author of the poster, A. Saha, was a post-doc and not a graduate student). The work has been presented as invited seminars at several institutions, typically at a rate of three a year. The latest presentations were made at Harvard University, at the General Electric's Global Research Center in Schenectady, NY and as a department seminar at RPI in Troy NY.

The grant supported the doctoral thesis research of S. R. Shah. He was further supported, partially, as a post-doctoral research associate. Additionally, Dr. Atanu Saha was also supported as a post-doctoral associate on this AFOSR grant.

The fundamental work on PDCs performed under this grant continues to have a broad impact on the research community. Efforts to enlarge both the size and the scope of research on these materials remains a high priority with the principal investigator. The PI has organized a series of three biannual workshops on ultrahigh temperature PDCs in Boulder, Colorado to achieve this broad objective. The next workshop is slated for the summer of 2004. A special issue on this topic, published in October 2001 in the Journal of the American Ceramic Society was yet another initiative to establish this field of research.

The significant pieces of work resulting from this grant have been published in papers which are listed immediately in the following section. Thereafter, these results are summarized to highlight the three key achievements: (a) the development of a pressure casting process for the fabrication of dense specimens and the measurement of basic mechanical properties of SiCN from these samples, (b) the experimental and theoretical description of nanoscale densification creep, and (c) the exhaustive work on fibers, including synthesis, the understanding of the mechanisms related to processing, and the measurement of mechanical properties and high temperature stability including the oxidation behavior. Among them, the work on fibers is deemed to have been the most important.

Publications

2001

- "Nanoscale Densification Creep in Amorphous Silicon Carbonitride", S. Shah and R. Raj, *J.Amer. Ceram. Soc.*, Vol. 84[10], 2208-12 (2001).
- "Oxidation Kinetics of An Amorphous Silicon Carbonitride Ceramic", Rishi Raj, Linan An, Sandeep Shah, Ralf Riedel, Claudia Fasel, and H-Joachim Kleebe, *J.Amer. Ceram. Soc.*, Vol 84[8], 1803-1810 (2001).
- R. Raj, R. Riedel and G. D. Soraru, *Special Issue of the J. American Ceramic Society on "Ultrahigh Temperature Polymer Derived Ceramics"*, Eds. R. Raj, R. Riedel and G. D. Soraru, *J.Amer. Ceram. Soc.*, Vol 84[10], pp 2158-2264 (2001).

2002

- "Mechanical Properties of a Fully Dense Polymer Derived Ceramic Made by a Novel Pressure Casting Process", S. R. Shah and R. Raj, *Acta Materiala*, Vol 50[16], 4093-4103 (2002).
- "Crystallization of Polymer Derived Silicon Carbonitride at 1873K under Nitrogen Overpressure", M. Friess, J. Bill, J. Golczewski, A. Zimmermann, F. Aldinger, R. Riedel, and R. Raj, *J.Amer. Ceram. Soc.*, Vol. 10, 2587-2589 (2002).
- "Pyrolysis Kinetics for the Conversion of a Polymer into an Amorphous Silicon Oxycarbide Ceramic", G. D. Soraru, L. Pederiva and R. Raj, *J.Amer. Ceram. Soc.*, Vol 85[9], 2181-2187 (2002).

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- "Amorphous Silicon Carbonitride Fibers Drawn from Alkoxide Modified Ceraset™", A. Saha, S. R. Shah and R. Raj, *J.Amer. Ceram. Soc.*, 86 [8]: 1443-1445 (2003).
- "Passive Oxidation of an Effluent System: the Case of Polymer Derived SiOC", S. Modena, G. D. Soraru, Y. Blum and R. Raj, submitted for publication.
- "Influence of the Distributed Particle Size on the Determination of the Parabolic Rate Constant for Oxidation by the Powder Method", S. R. Shah, A. Saha and R. Raj, *J.Amer. Ceram. Soc.*, Vol. 86[2], 351-353 (2003).
- "Oxidation Behavior of SiCN-ZrO₂ Fiber Prepared from Alkoxide Modified Silazane", A. Saha, S. R. Shah and R. Raj, Submitted to *J. Amer. Ceram. Soc.*, October 2003.

Patent

"Nanocomposite Ceramics of Oxide and Non-Oxide Phases and Methods for Producing Same", Atanu Saha, Sandeep Shah and Rishi Raj, U.S. Patent filed May 8, 2002.

Summary of Results

Preamble

It is important to recognize that the PDCs are materials of ternary compositions. The present study has concentrated on ceramics made from silicon carbon and nitrogen, or SiCN. Furthermore, the unusual properties of SiCN (resistance to creep and crystallization at ultrahigh temperatures) are achieved only if the compositions have excess carbon relative to stoichiometric mixtures of the crystalline phases of silicon nitride and silicon carbide. In other words, simple alloys of Si_3N_4 and SiC will easily crystallize at temperatures where SiCN remains "amorphous". However, as shown in Fig. 1, the characteristic properties of the PDCs are obtained over a wide range of carbon content as long as the compositions lie above the tie line connecting Si_3N_4 and SiC. Recent work is starting to show how this excess carbon may be controlling the nanostructure of the PDCs in a way that leads to their unusual properties at ultrahigh temperatures.

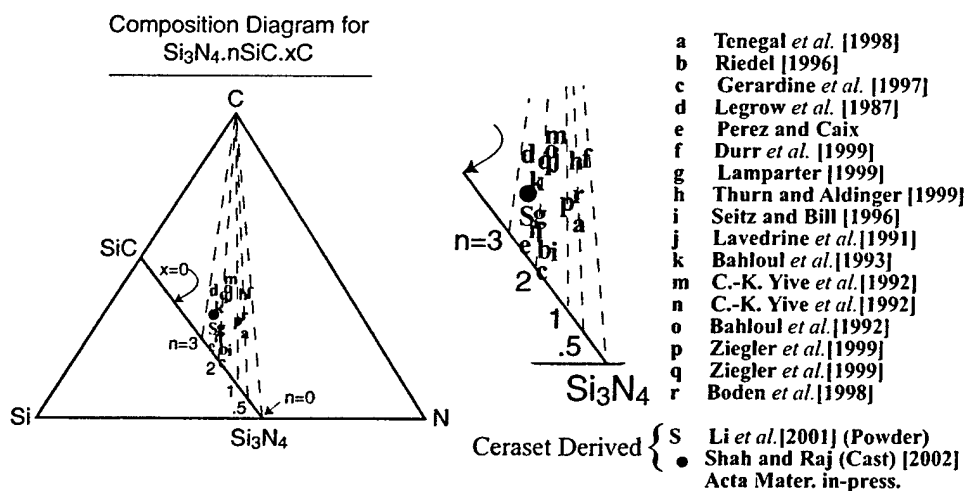


Figure 1: The range of compositions where SiCN can be obtained in the amorphous form. The PDCs nearly always contain excess carbon since their composition lies above the tie line connecting stoichiometric SiC and Si_3N_4 .

A. Mechanical Properties of a Fully Dense Polymer Derived Ceramic Made by a Novel Pressure Casting Process

The PDC process is radically different from conventional processing of ceramics. Conventionally, ceramic bodies are made by sintering of crystalline powders, at relatively high temperatures, typically at $0.75T_M$ where T_M is the melting point. For example zirconia must be

sintered at about 1400°C, and silicon nitride at an even higher temperature. In contrast the PDC process comprises of crosslinking a liquid precursor into a rigid plastic which is then immediately pyrolyzed to yield the ceramic phase. The entire process is completed well below 1000°C. During pyrolysis hydrogen is evolved leaving behind a refractory compound of carbon, silicon and nitrogen.

While the polymer process does yield a material with unusual properties, scientific investigations of these properties were thwarted by the inability to fabricate dense specimens, the issue being that the volatiles released during the pyrolysis caused the body to dilate and microcrack. In the past [1-2] the problem of cracking was circumvented by crushing the crosslinked organic polymer into powder, pressing the powder into a shape followed by pyrolysis. The interparticle pores permitted the effusion of the volatiles without causing the object to develop cracks. However, the final ceramic remained highly porous.

The research at Colorado has been successful in fabricating samples which are fully dense. The key feature of this process is that the organic liquid is cross-linked into a polymer under hydrostatic pressure. This pressure casting process apparently creates a molecular network which resists cracking during pyrolysis. These results are described in Fig. 2.

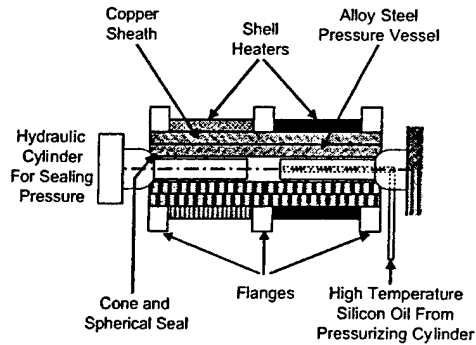
The mechanical properties of the pressure cast SiCN samples are also described in Fig. 2. The graph given at the bottom shows the measurement of the hardness, while the graph on the right hand side gives the Weibull plots for the fracture strength. In this graph the fracture strength of the pressure cast specimens is compared to the specimens made by the powder process [1-2]. The cast specimens show a much higher strength. Surface polished specimens made by the pressure casting route have an average strength of 1 GPa with a Weibull modulus of 12.

In addition to the hardness and the fracture strength, the Youngs Modulus of the cast specimens was measured by three different methods. All gave a consistent value in the range 160-180 GPa. Therefore the hardness to modulus ratio of amorphous SiCN is two to three time larger than for crystalline silicon nitride and silicon carbide. This is a surprising result which reflects on the unusual nanostructure of polymer-derived SiCN.

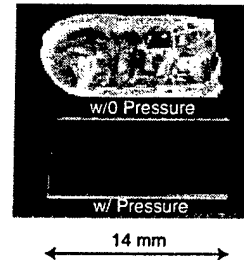
B. Nanoscale Densification Creep

There are now several studies of high temperature creep in SiCN ceramics that have been published in the literature [3-5]. These studies have consistently shown that SiCN exhibits a declining creep rate at ultrahigh temperatures, eventually to imperceptible levels. In other words, the PDCs have unusually high resistance to creep. Their creep performance is far superior to that of conventional engineering ceramics made from polycrystalline silicon nitride and silicon carbide.

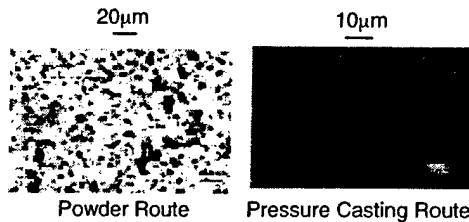
Nevertheless, the PDCs do exhibit *transient* creep which still remains unexplained. The



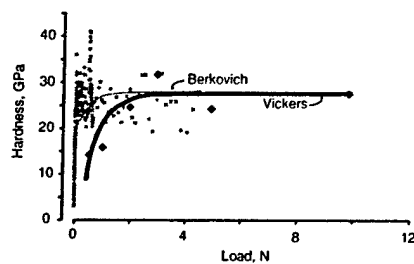
The pressure casting apparatus built at the University of Colorado



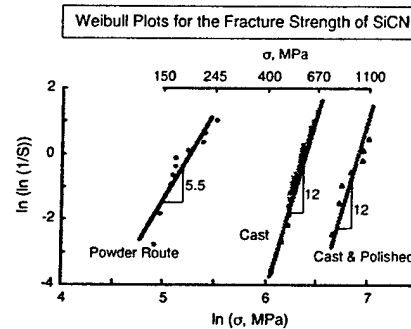
A specimen cross-linked at ambient pressure (top), and at 60 MPa in the pressure casting apparatus (bottom).



Optical metallographs of specimens prepared by the powder and the pressure casting routes.

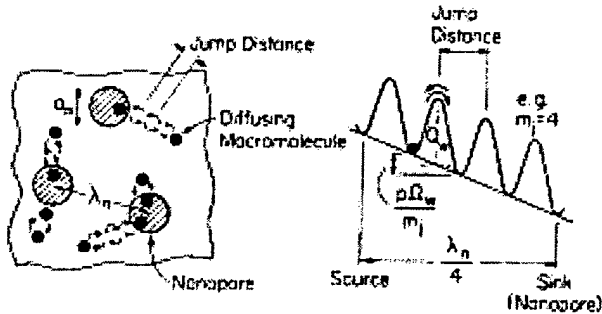
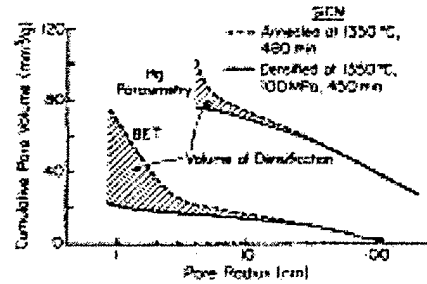
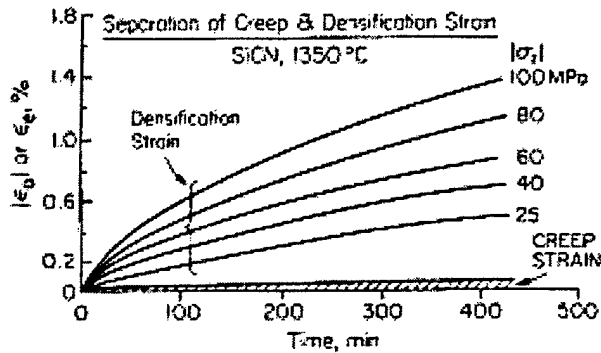


Hardness of cast SiCN specimens measured by two different indentation techniques.



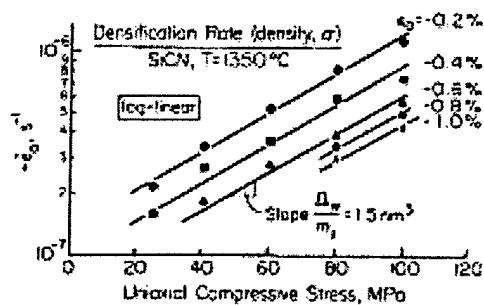
Weibull plots of the fracture strength of specimens prepared by the powder and the pressure casting routes. Surface polish of the cast specimens leads to fracture strengths as high as 1.1 GPa.

Figure 2: A summary of the pressure casting process and the fracture and hardness of the SiCN specimens made by this process. The top right picture shows the polymer specimens made with and without the pressure annealing. The metallographs in the middle compare the specimens prepared by the powder process and by the new pressure casting process. The hardness measurement and the fracture strength of cast specimens are shown just above..



- Jump Frequency k_w
- Molecular Volume Ω_w
- Molecule Size $n_w = \Omega_w^{1/3}$
- Jump Distance = Molecular Size
- Diffusion Distance = Pore Spacing(λ_n)/4
- Pore Size

Model for the Densification Rate



$$\dot{\rho} = \left\{ \frac{1}{\lambda_n^3} \right\} \left\{ \Omega_w (n_w \lambda_n^3) \frac{k_w q}{m_1} \right\}$$

\uparrow # Nanopores per unit Volume \uparrow Molecular Volume \uparrow # units entering single pore \uparrow arrival rate of oligomer at pore

Diffusion of molecules in pores per unit time

$$\dot{\rho} = \frac{A_w D_w}{\lambda_n \Omega_w^{1/3}} e^{-\frac{\sigma \Omega_w}{6 m_1 k T}}$$

Figure 3: Results from the study of shear and densification creep determined from the measurement of axial as well as the radial strains. Surprisingly the shear creep is absent, highly unusual for a materials with an ostensibly amorphous structure. The densification behavior was related to the closure of nanoscale pores which requires only short range molecular diffusion. The model agreed well with the data and yielded a size for the diffusing molecular unit: 1.2 nm. (Shah and Raj, Ref. 8)

Colorado work had provided an explanation for this transient creep: it showed that the transient creep results from the closure of nanoscale pores within the material. This conclusion is reached from experiments where shear creep (which results from change in shape without a change in the volume of the material) and densification creep (which accounts only for the change in volume) are measured simultaneously. The technique consists of measuring both the axial as well as the radial rate of deformation in cylindrical upright specimens and then using well established equations to separate the shear and the densification strain.

The results, which are described in Fig. 3, show that all the transient strain is accounted for by densification creep. Furthermore, the densification strain was accompanied by the closure of nanoscale pores. A kinetic model for densification was successfully applied to the data. In this model the densification is produced by a few discreet jumps of molecular units under the influence of the applied stress. The comparison of theory and experiment gave an estimate of 1.2 nm for the size of the diffusing molecules.

The large size of the diffusing unit (1.2 nm) is significant because it explains why self diffusion in these materials is apparently very slow. The PDCs show great resistance to crystallization at ultrahigh temperatures. This resistance can be explained either by a high barrier to the nucleation of crystallites or from slow mobility of molecules in the solid state which is required for the growth of the crystallites. High resolution transmission electron microscopy images of PDCs are generally non-descript but they often show the presence of a few crystallites of silicon carbide. The fact that there is negligible progress towards crystallization despite the presence of these nuclei implies that the resistance to crystallization arises most likely from the low mobility of the molecular species.

The understanding of the detailed mechanisms of diffusion in the PDCs remains one of the most fascinating scientific question. The present work strongly suggests that the rate of diffusion is very slow, and it highlights the need for elucidating the nanostructural origins of this very interesting phenomenon.

C. PDC Fibers made of a Oxide-Nonoxide (SiCN-ZrO₂) Ceramic

The results on PDC-fibers represent the most significant achievements in this AFOSR Grant. A novel process for the synthesis of ultrahigh temperature fibers from polysilazane was invented: the key elements of the process are described in Fig. 4. The thermal stability and the mechanical properties of these fibers are summarized in Fig. 5 and 6. The oxidation behavior is given in Fig. 7. The stability of the nanostructure is shown in Fig. 8. These results are described in greater detail in the following paragraphs. We begin by comparing the engineering properties of the PDC fiber and other, polycrystalline silicon carbide and silicon nitride fibers. The fracture strength, the Youngs modulus (E), the temperature for the onset of thermal decomposition (T.S.) and the magnitude of the parabolic rate constant for oxidation at 1350°C, k_p , are compared in Table I.

Table I

Properties of SiCN-ZrO₂ and expensive Hi-Nicalon fibers are compared.

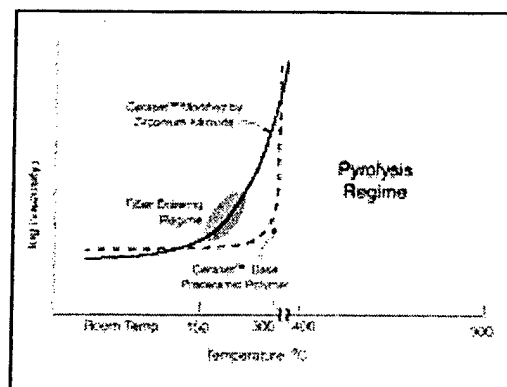
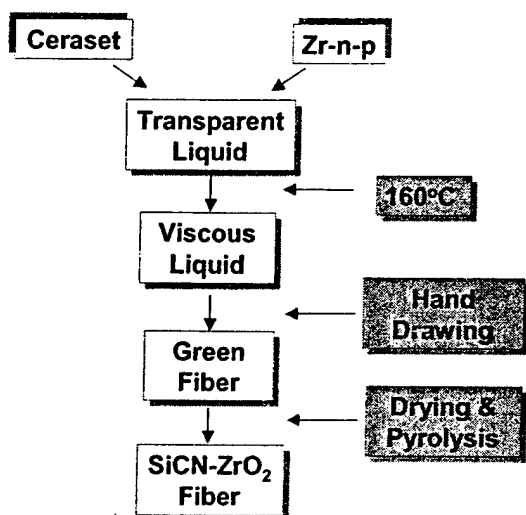
Fiber	Strength (GPa)	E (GPa)	T. S. (°C)	$k_p \times 10^{18}$ (m ² /sec) 1350°C
Nicalon	2.1	120	1200	11
Hi-Nicalon	3	285	1600	18
EB-SiC	2	270	1600	14.1
SiCNO	1.8-2.5	220	1400	10.14
SiCN-ZrO ₂	2.2-2.8	160-190	1450	16.4

The results in Table I show that the PDC (SiCN-ZrO₂) fiber is better than Nicalon, but not as good as Hi-Nicalon and EB-SiC fibers. The principal difference between them lies in the thermal stability at high temperatures. The Hi-Nicalon and EB-SiC fibers have the highest thermal stability, with the onset of decomposition taking place at approximately 1600°C. The PDC fiber has the next highest stability temperature of 1450°C. The Hi-Nicalon and EB-SiC fibers are highly stable because they are very pure: the presence of even small amounts of oxygen will lower its decomposition temperature. For example, Nicalon which contains some oxygen begins to decompose at only 1200°C. In comparison the PDC-fiber is much more stable even though it contains significant amounts of oxygen. The high intolerance of silicon carbide based fibers (EB-SiC and Hi-Nicalon) to oxygen and the remarkable tolerance of SiCN fibers to the presence of oxygen suggests that the PDC-fibers have a fundamentally different structure than the silicon-carbide based fibers. The reason for this difference remains an important question in the evolution of the science and the technology of these novel PDC materials.

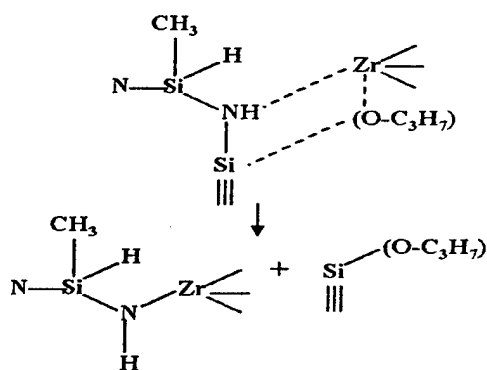
The most important difference between PDC and the other fibers lies not so much in the properties as in the cost of processing. The high sensitivity of silicon carbide-based fibers to oxygen means that great care must be taken to maintain a highly inert, oxygen free environment during the entire process. In contrast the PDC-fibers can be processed in ambient environment, at least for the most part. Thus the process schedule for PDC-fibers is much more benign and forgiving. The cost of manufacturing the PDC-fibers, therefore, is also likely to be much, much lower.

The key feature of the process invented at the University of Colorado, is the modification of the rheological behavior of the silazane precursor (Ceraset™) by the addition of a zirconium alkoxide as sketched in the upper right hand in Fig. 4. In the unmodified precursor, the viscosity changes abruptly from that of a fluid liquid (more or less like water) to a highly cross-linked solid as the temperature is raised. By adding small amount of the alkoxide the rheology increases gradually with temperature, thus opening up a processing window where the viscosity is suitable

The PDC-Fiber Invention



Modification by Alkoxide alters viscosity of Silazane amenable to fiber drawing.



Zr forms donor-acceptor bond with nitrogen, followed by rupture of Si-N.

Figure 4: The invention lies in changing the rheology of the polysilazane based Ceraset, which is the precursor for SiCN, so that it becomes amenable for fiber drawing. This is achieved by modifying the precursor with zirconium isopropoxide, itself a precursor for the oxide, zirconia. The proposed mechanism for the change is rheology is illustrated on the bottom right.

for fiber drawing. The molecular mechanism for the change in rheology is not clearly understood, but it is expected to arise from the scission of the ring structures in the polysilazane (which lead to rigidity) into linear chain like structures which help to retain some degree of fluidity even after thermal cross-linking. This mechanism is currently being investigated by measuring the change in the IR spectra of the polymer mixture as a function of the temperature.

The fibers produced by the above process have smooth, glass-like surfaces as shown in Fig. 5. Wide angle x-ray diffraction analysis of the material shows essentially amorphous structure (later work with small angle x-ray scattering, which is not reported here, shows the presence of nanoscale clusters or domains, that is, these materials are not strictly amorphous but contain a significant degree of short range order).

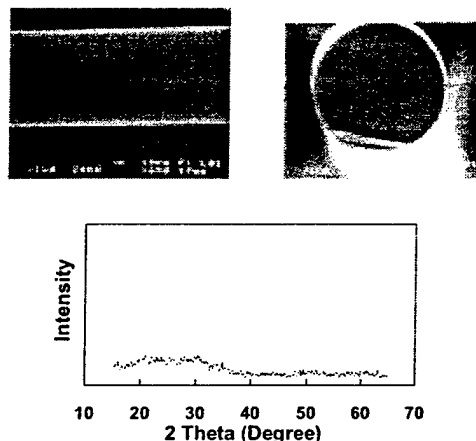
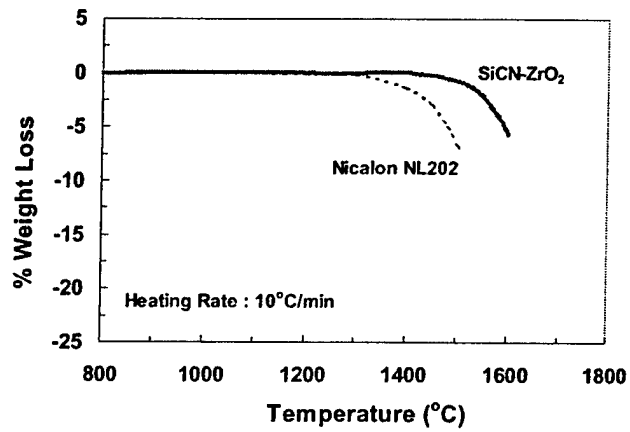


Figure 5 The fiber is amorphous having chemical composition
 $\text{SiZr}_{0.13}\text{C}_{0.461}\text{N}_{0.785}\text{O}_{0.69}$

When pulled in tension the PDC-fibers fracture from a defect on the surface of the fiber, typically a dust particle. Therefore reducing the surface area (by reducing the diameter of the fibers) or processing the fibers in a clean room can produce a significant increase in the fracture strength (by reducing the probability of finding a defect). Indeed, the fracture strength is found to increase significantly as the fiber diameter is reduced as shown by the results given on the bottom right hand corner in Fig. 6. This figure also shows a comparison of the TGA data for the present fibers and the Nicalon fibers in the upper left hand corner.

Oxidation resistance is another "go-no-go" property of the fibers for high temperature structural applications. It is appropriate to compare the oxidation kinetics of SiCN with that of polycrystalline silicon carbide and silicon nitride. The crystalline materials have been shown to have highly variable oxidation with the parabolic rate constant varying over three orders of

Thermal Stability at Ultrahigh Temperatures



Young's Modulus and Fracture Strength

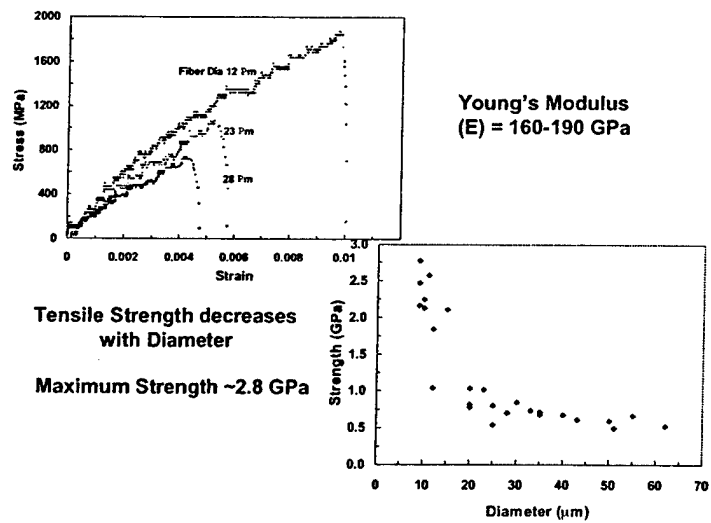
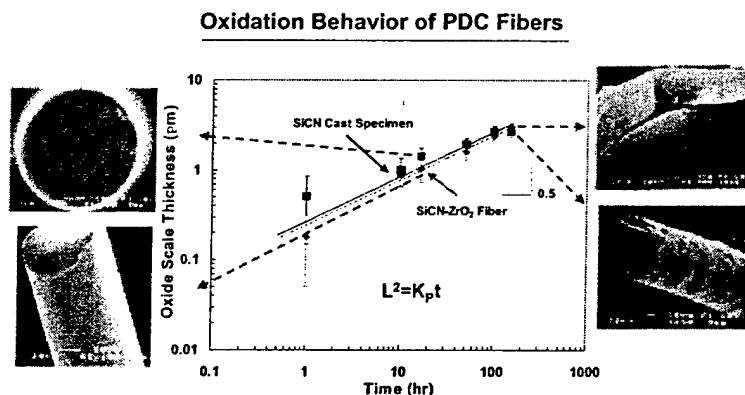


Figure 6: High Temperature Stability and Mechanical Properties of PDC-Fiber

magnitude. This variability is ascribed to the impurities in the grain boundary phase which lowers the viscosity of the passivating silica overgrowth. Not surprisingly the lowest oxidation rates in the polycrystalline materials are obtained when the materials are very pure having been prepared by a chemical vapor deposition process. Surprisingly, the oxidation kinetics of SiCN is comparable to the oxidation kinetics of CVD silicon carbide even though SiCN contains a significant amount of oxygen as an impurity. In the present work we have compared the oxidation kinetics of simple SiCN and the fibers which are made of SiCN-ZrO₂. These results are shown in Fig. 7. The measured rate constants, given by the slope of the lines in Fig. 7, are nearly the same for both materials, which shows that the addition of zirconia to SiCN does not significantly affect its oxidation rate. However, if the rate of growth of the silica overlayer is corrected for the presence of oxygen within the parent material, it is found that the fiber material has a lower rate constant for oxidation than SiCN. The lower activity of carbon in the fiber material, which is expected to have raised the oxygen activity at the interface between the substrate and the overgrowth, is given as the explanation for the lower oxidation rate of SiCN-ZrO₂ polymer derived ceramic.

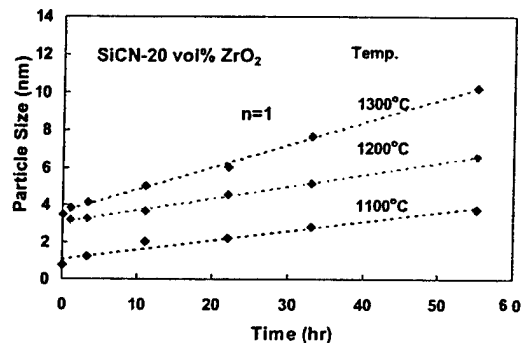


Parabolic growth of oxide layer indicating diffusion controlled oxidation.

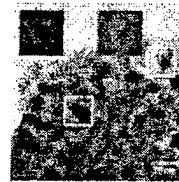
Figure 7: The oxidation kinetics of the PDC-Fiber and its comparison to the oxidation behavior of pressure cast SiCN specimens. Both materials have very similar oxidation behavior suggesting that the addition of the oxide (zirconia) does not degrade the oxidation resistance of the PDC.

Finally, we have embarked upon the study of the nanostructure of SiCN-ZrO₂. High resolution transmission electron microscopy has shown that zirconia is distributed as nanoscale crystallites as shown in the micrograph in Fig. 8. The coarsening rate of these particles appears to fit an interface controlled (as opposed to diffusion controlled) reaction mechanism. These early data are also given in Fig. 8. These measurement are eventually expected to provide information regarding the fundamental transport mechanisms in the PDCs.

Interface controlled growth of ZrO_2 in amorphous SiCN.



$$D^n - D_0^n = Kt$$



1300°C/10h

Figure 8: The nanostructure of the PDC-fiber consists of a SiCN matrix containing a nanoscale dispersion of zirconia crystallites. The graph on the left shows the rate of coarsening of these fine precipitates with time and temperature.

Summary

In summary, this AFOSR grant is deemed to have been successful in achieving its objectives. A novel process was invented to draw fibers from SiCN. The fibers have been shown to have properties which are better or nearly comparable to the silicon carbide-based fibers. However, the PDC process is more benign and forgiving, and therefore much more cost-effective than the current process used to make Hi-Nicalon and EB-SiC fibers. A comparison of the phenomenological properties of the PDC and non-PDC materials is beginning to suggest that the PDCs have a unique nanostructure which underlies their unusual properties. The AFOSR work has led to insights into the nanostructure of the PDCs.

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